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GHENT UNIVERSITY

FACULTY OF ENGINEERING AND ARCHITECTURE

Ab initio based microkinetic modelling as a tool to understand and improve controlled polymerization processes

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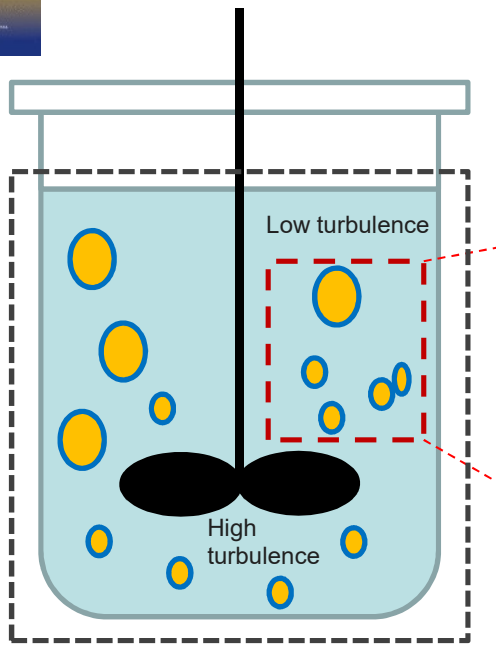
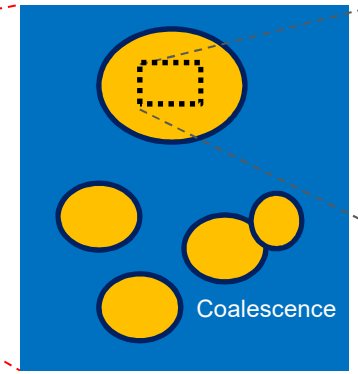
Overview

- Introduction: ab initio based multi-scale modelling
- Proof of principle: RAFT polymerization of styrene
    - computational method: model assumptions
    - validation of computational method
- Design of sequence controlled copolymers
- Insight in monomer sequence formation in gradient copolymers
- Conclusions

Multi-scale modelling: polymerization processes

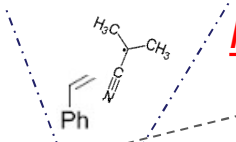


MACRO-SCALE



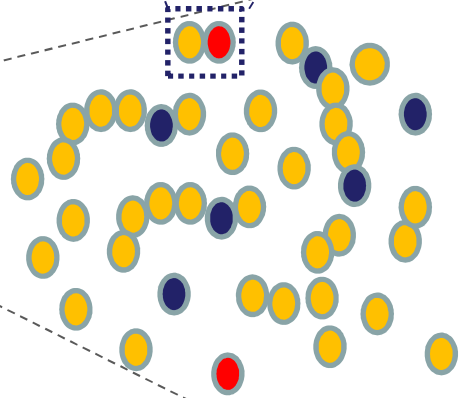
MESO-SCALE

MOLECULAR SCALE



Reaction

Molecular diffusion



MICRO-SCALE

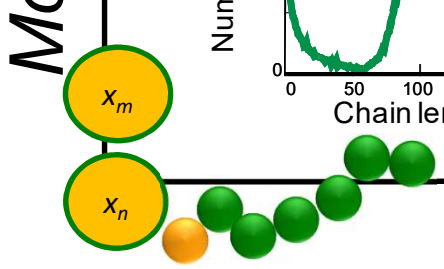
D'hooge et al., Progress in Polymer Science, 58, 59-89, 2016

Generic modelling toolkit

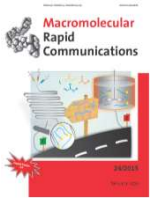
Model complexity

x_m

x_n

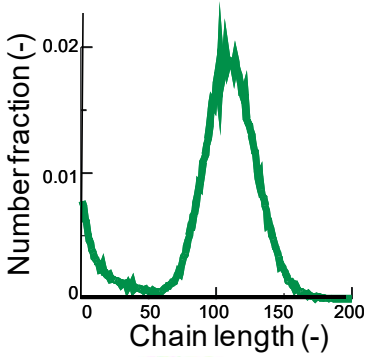


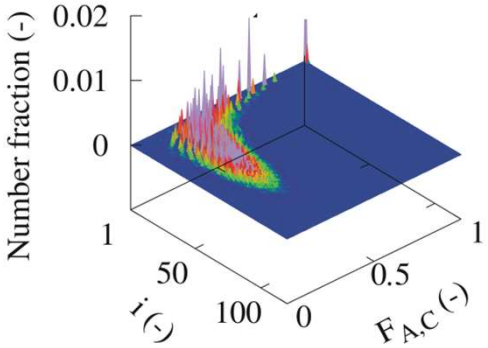
Macromolecular structural detail



copolymer composition
chain length distribution

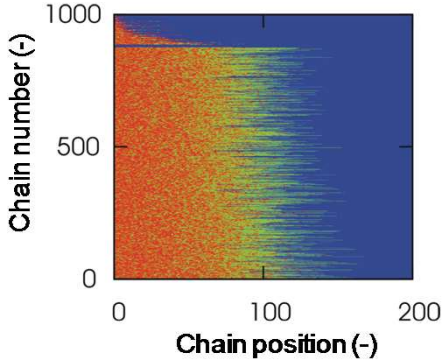
chain length distribution





Van Steenberge P.H.M. et al. Macromolecules 2011, 44, 8716.
Van Steenberge P.H.M. et al; Chem. Eng. Sci. 2014, 11, 185.
D'hooge D.R. et al. Polym. Chem. 2015, 6, 7081.
D'hooge D.R. et al. Prog. Polym. Sci. 2016, 58, 59

full microstructural detail
for each macrospecies

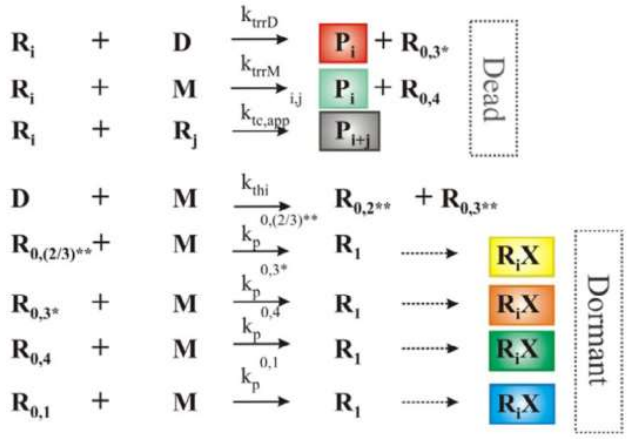


Van Steenberge P.H.M. et al.
Macromolecules 2012, 45,8519.

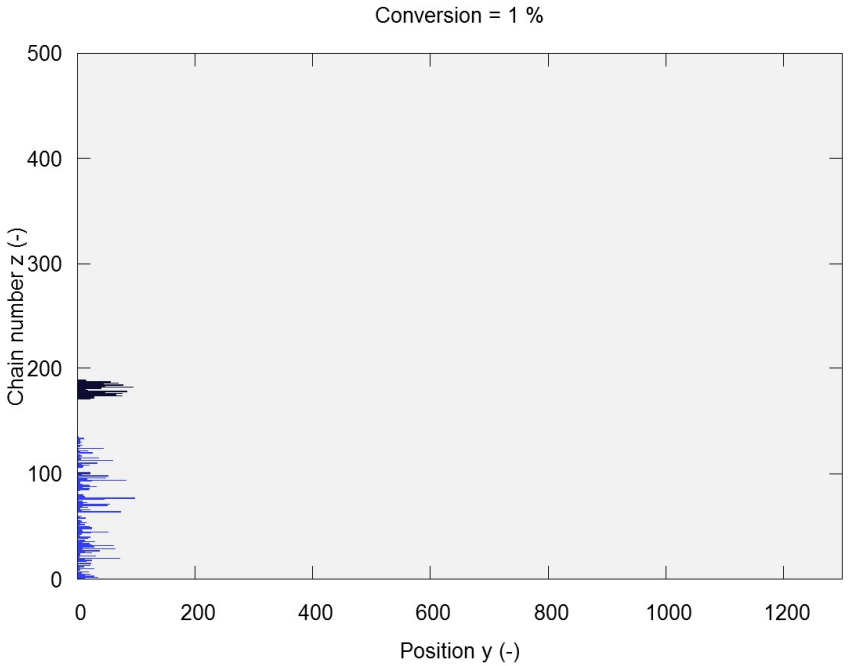
Matrix-based kinetic Monte Carlo algorithm

Blockbuilder-MA mediated polymerization of syrene (including all side reactions)

- tracking all reaction events leading to formation of each macromolecule (10^5 macromolecules)
- visualization: differentiation of macromolecules according to initiation/termination mechanism



- data analysis: loss of control (Đ↗ and EGF↘) mainly due to thermal initiation and chain transfer to dimer

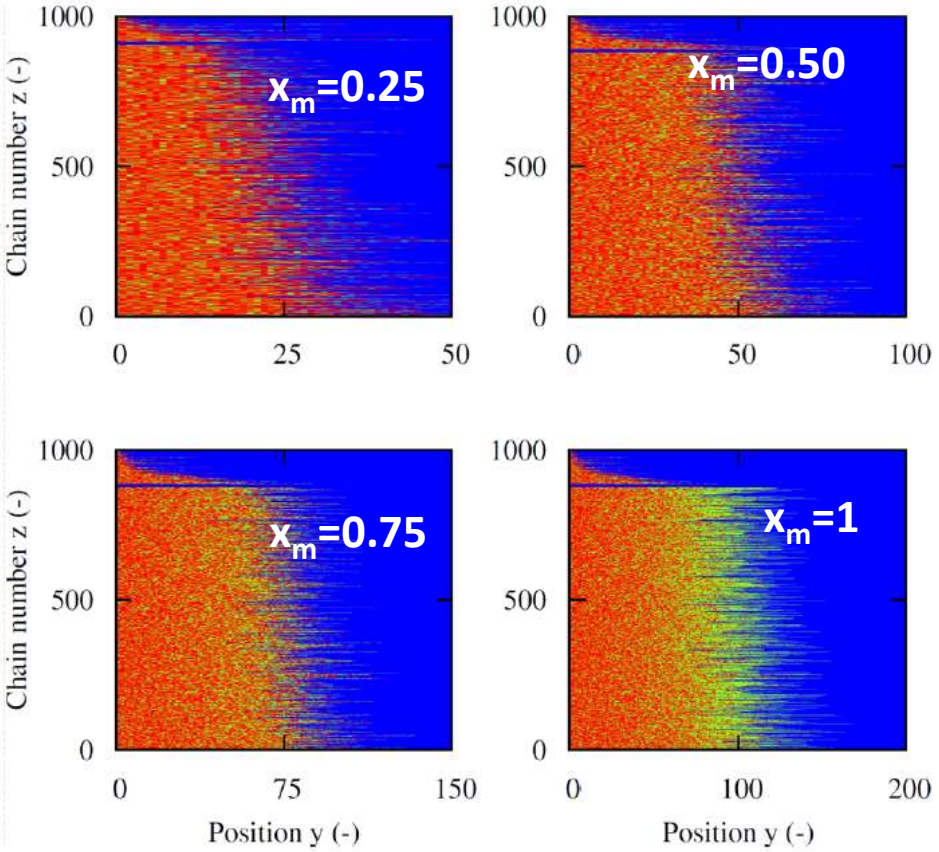


T = 120°C; TCL = 1000

Fierens et al., Chemical Eng. J. 278 (2015), 407-420

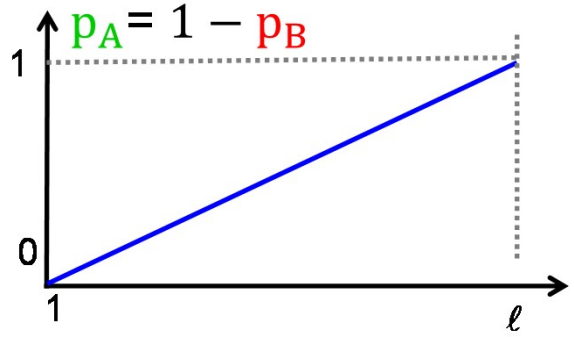
Linear gradient copolymers

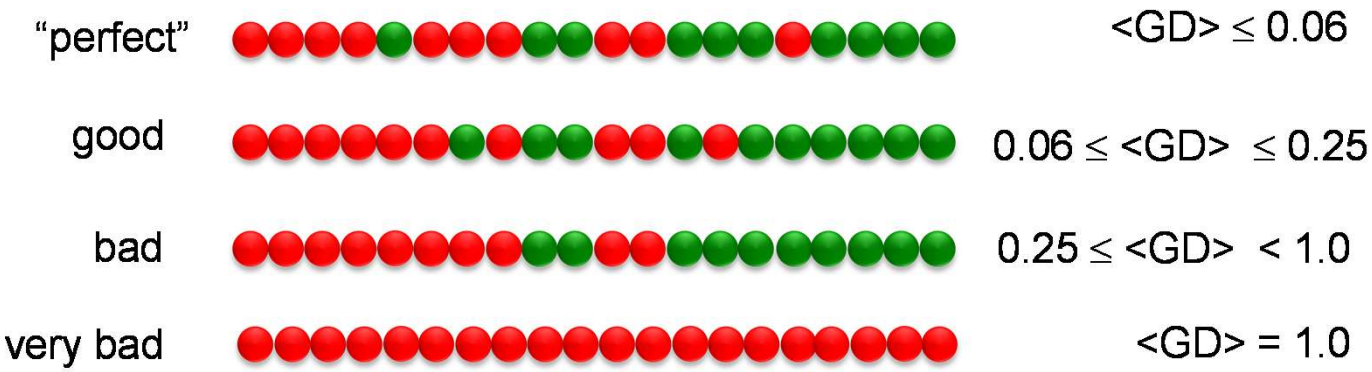
linear gradient copol
n-BuA/MMA via ATRP



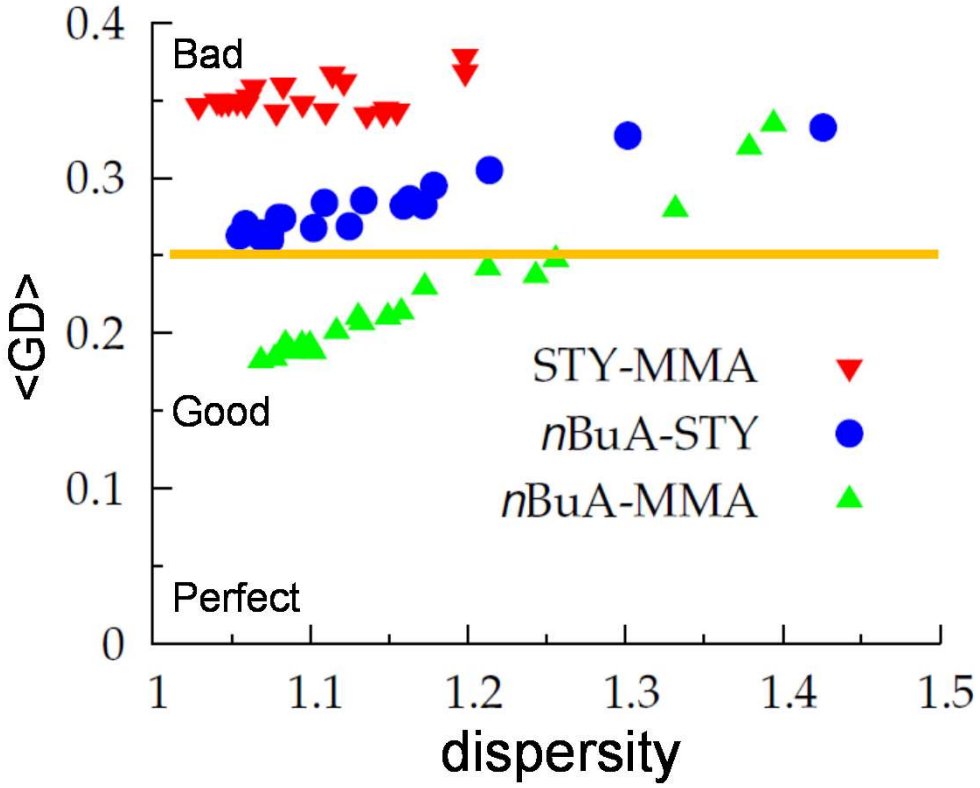
Classification of gradient quality via <GD> value

- Mathematical definition of ***perfect linear gradient chain***



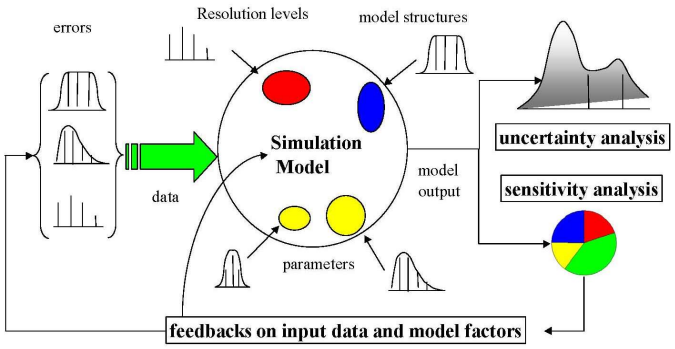


<GD> correlates with dispersity

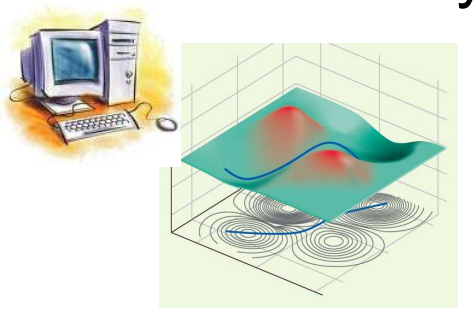


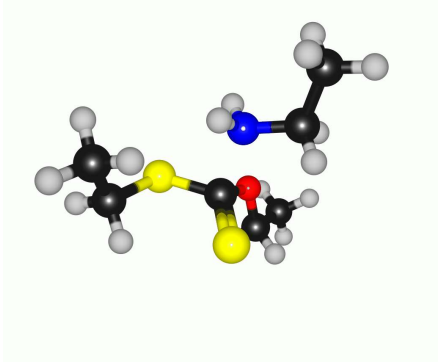
Kinetics elementary reactions

- experiment

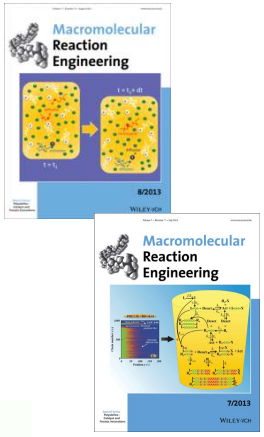


- quantum chemistry



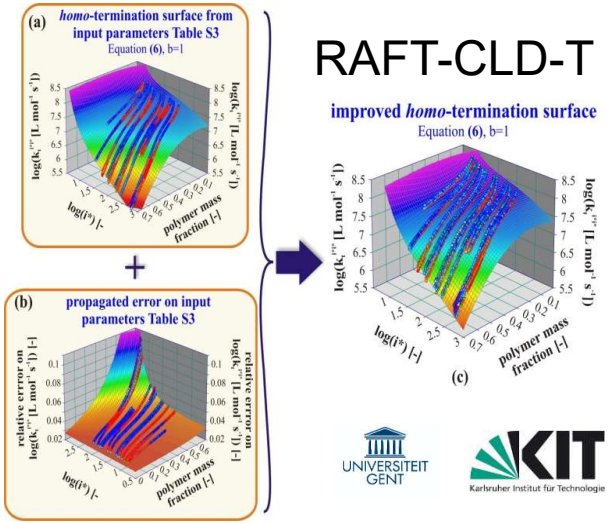


Including molecular diffusion



$$\frac{1}{k_{a,app}} = \frac{1}{k_{a,chem}} + \frac{1}{K_{eq}k_{da,diff}}$$

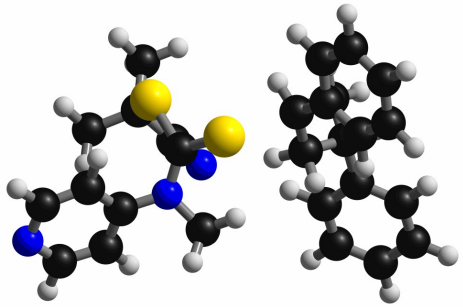
$$\frac{1}{k_{da,app}} = \frac{1}{k_{da,diff}} + \frac{1}{k_{da,chem}}$$



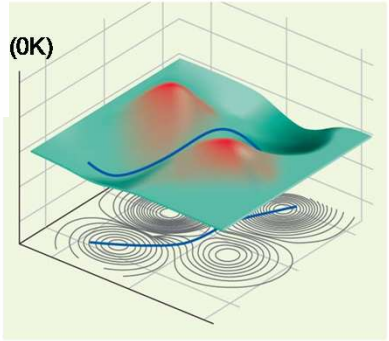
RAFT-CLD-T

Derboven et al. Macromolecules 2015, 48, 492

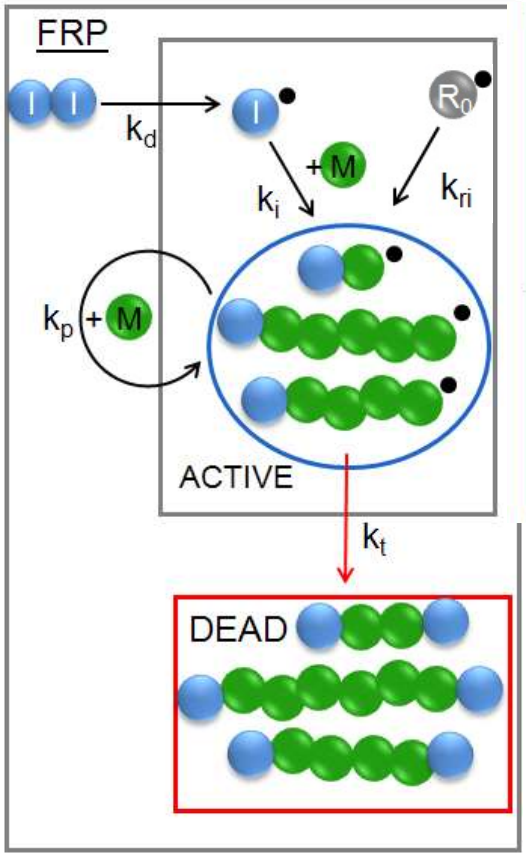
Ab initio based multi-scale modelling: approach

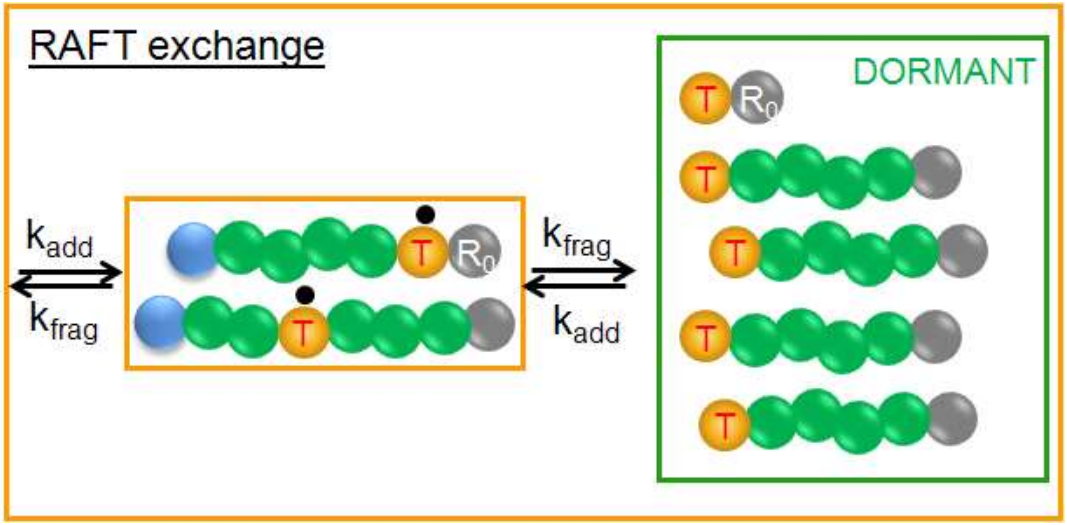


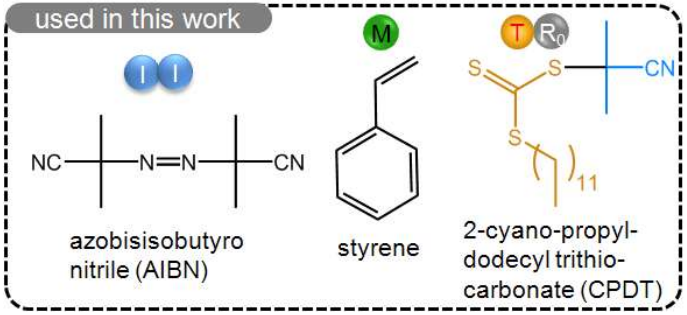
trade off between:
- accuracy
- computational cost

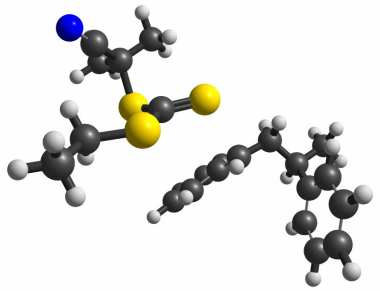


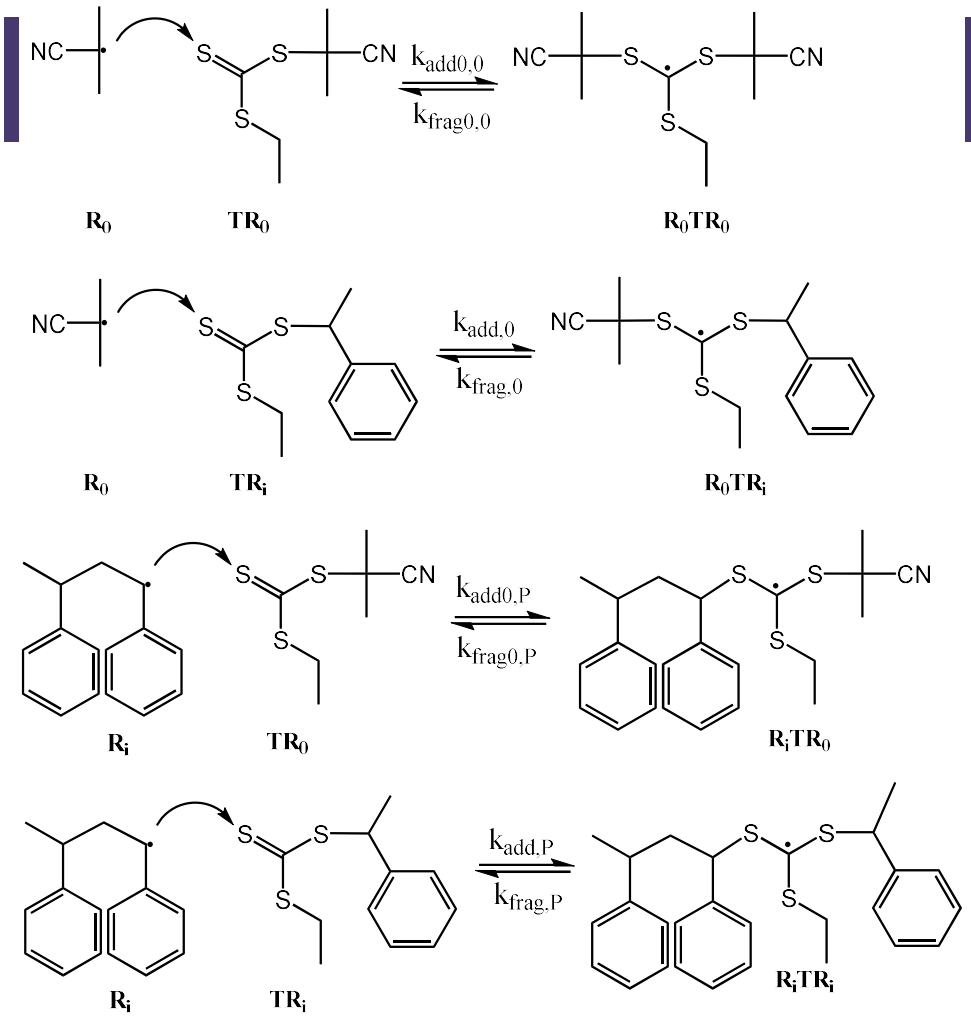
Proof of principle: RAFT of styrene











Computational method

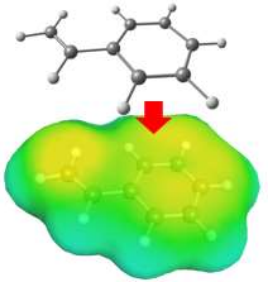
Model assumptions

- dimer radical to model macroradical[a]
- ethyl group to model dodecyl group

Ab initio calculation

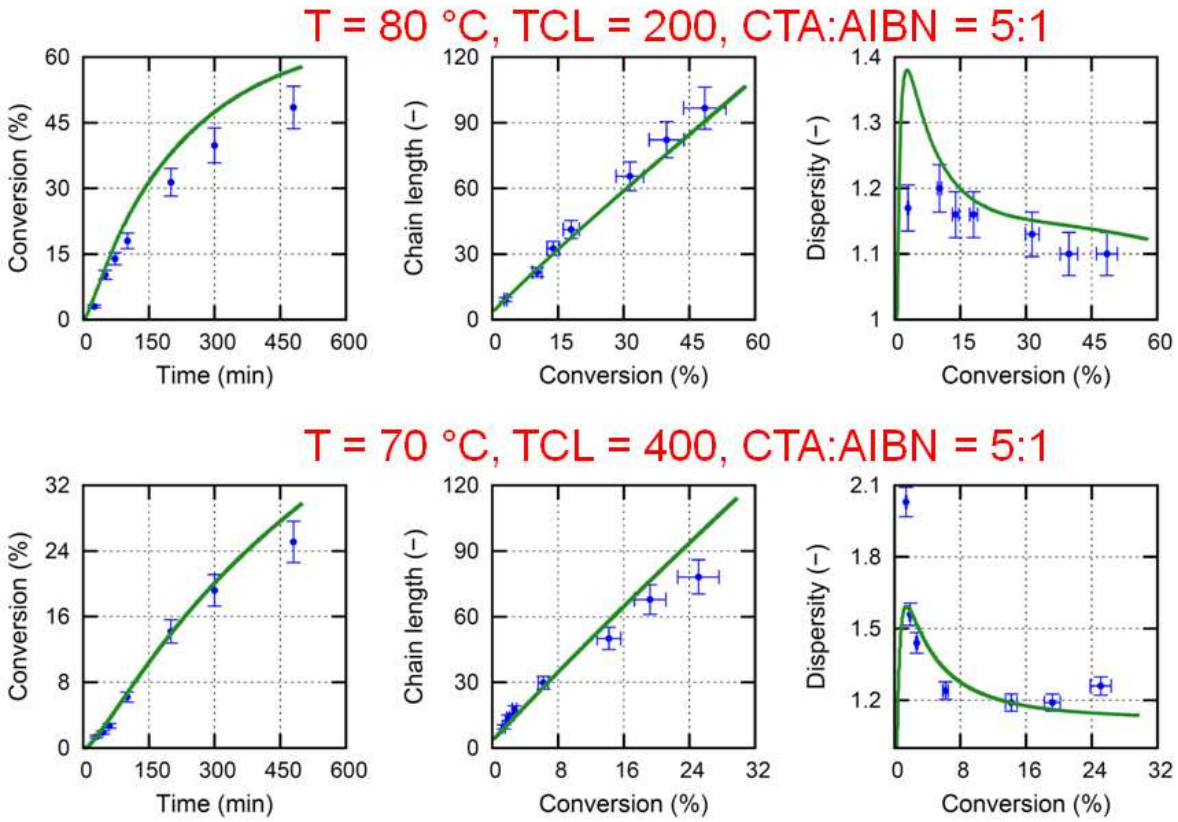
- scan conformers: B3LYP/6-31G(d)
- geometry optimization and frequencies: B3LYP/6-31G(d)
- 'single point' electronic energy: M06-2X/6-311+G(d,p)

Solvation via COSMO-RS



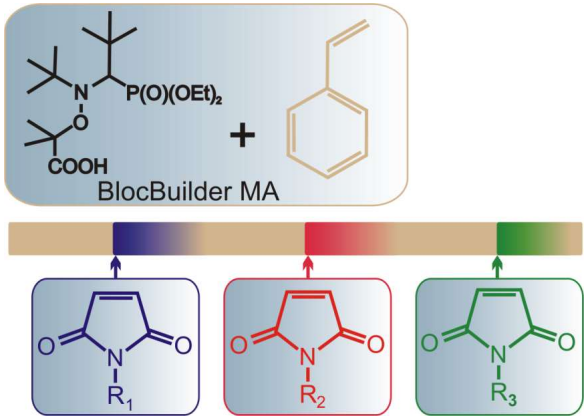
[a] *Lin and Coote, Aust. J. Chem. 2011, 94, 747*

Ab initio based microkinetic modelling



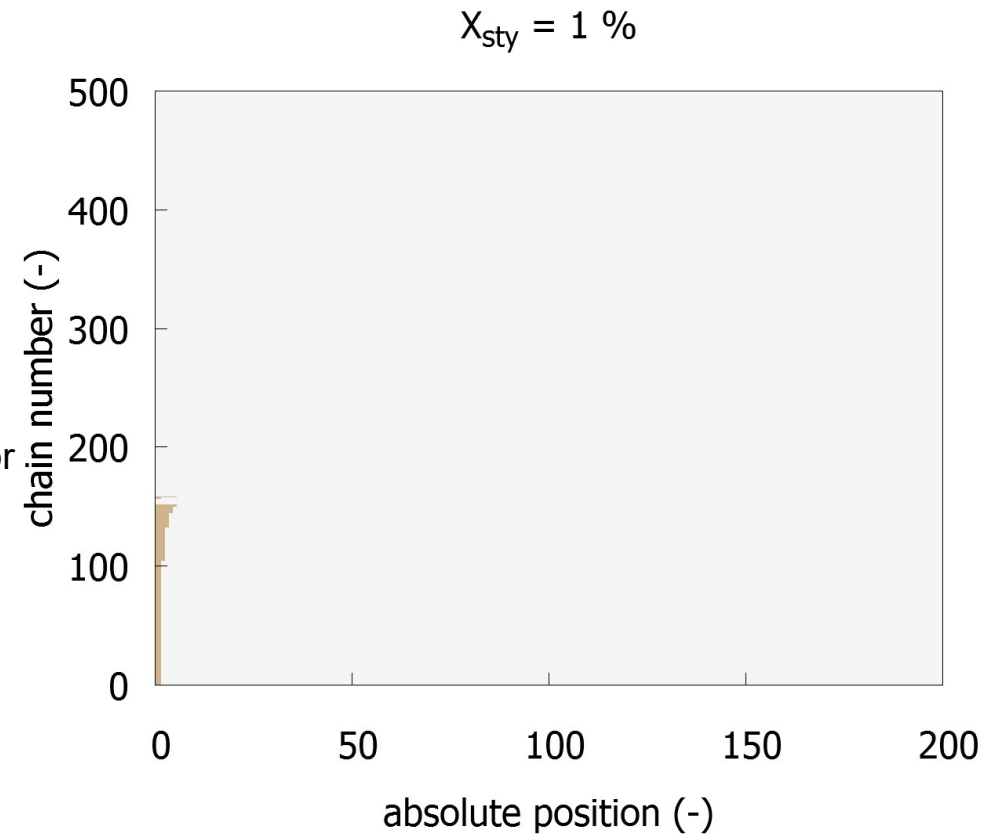
- very good agreement with experimental data in broad range of conditions
- computational approach validated

Model-based design: sequence controlled polymers



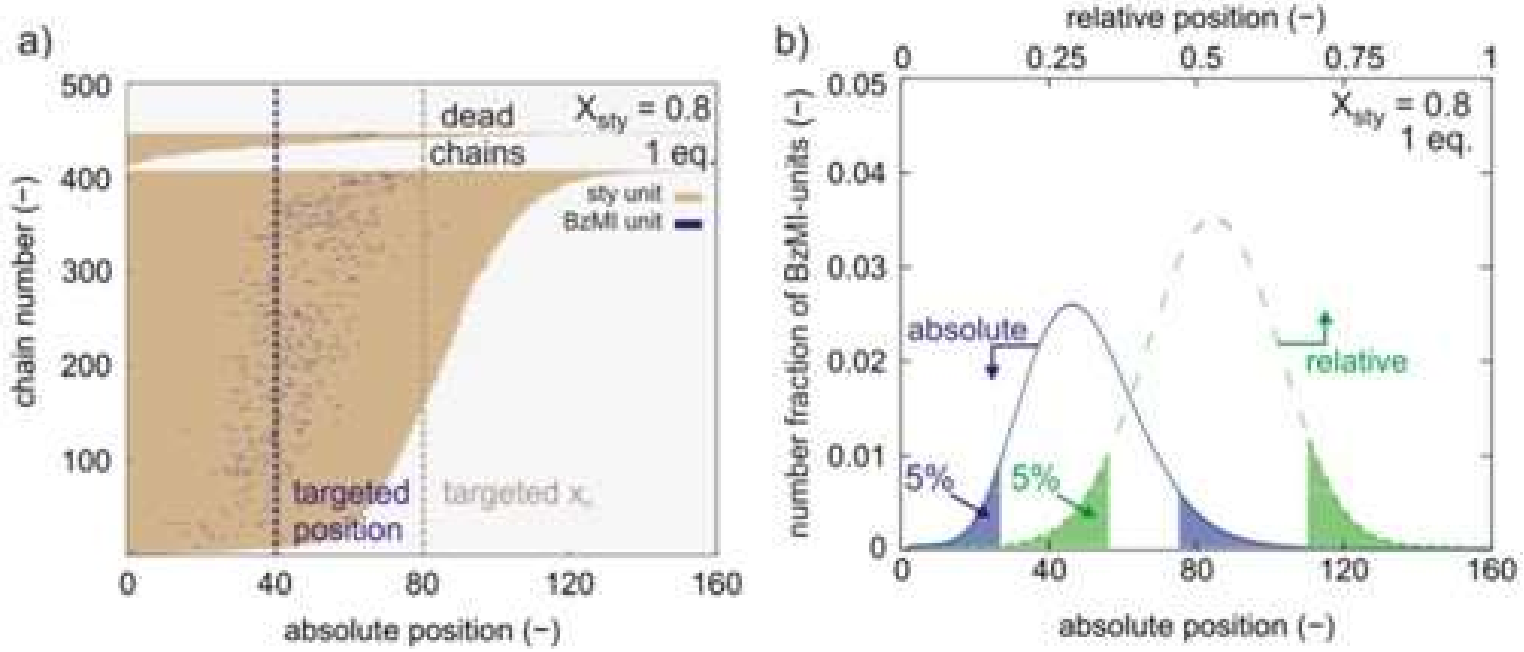
- Electron-donor (e.g. styrene) and electron–acceptor (e.g. N-substituted maleimide) comonomers
  - high cross-propagation
  - allows 'local' functionalization using CRP techniques
- CRP techniques are statistical processes: uncertainty of functional monomer placement

In collaboration with Dr. J.-F. Lutz



Design of monomer addition program (1)

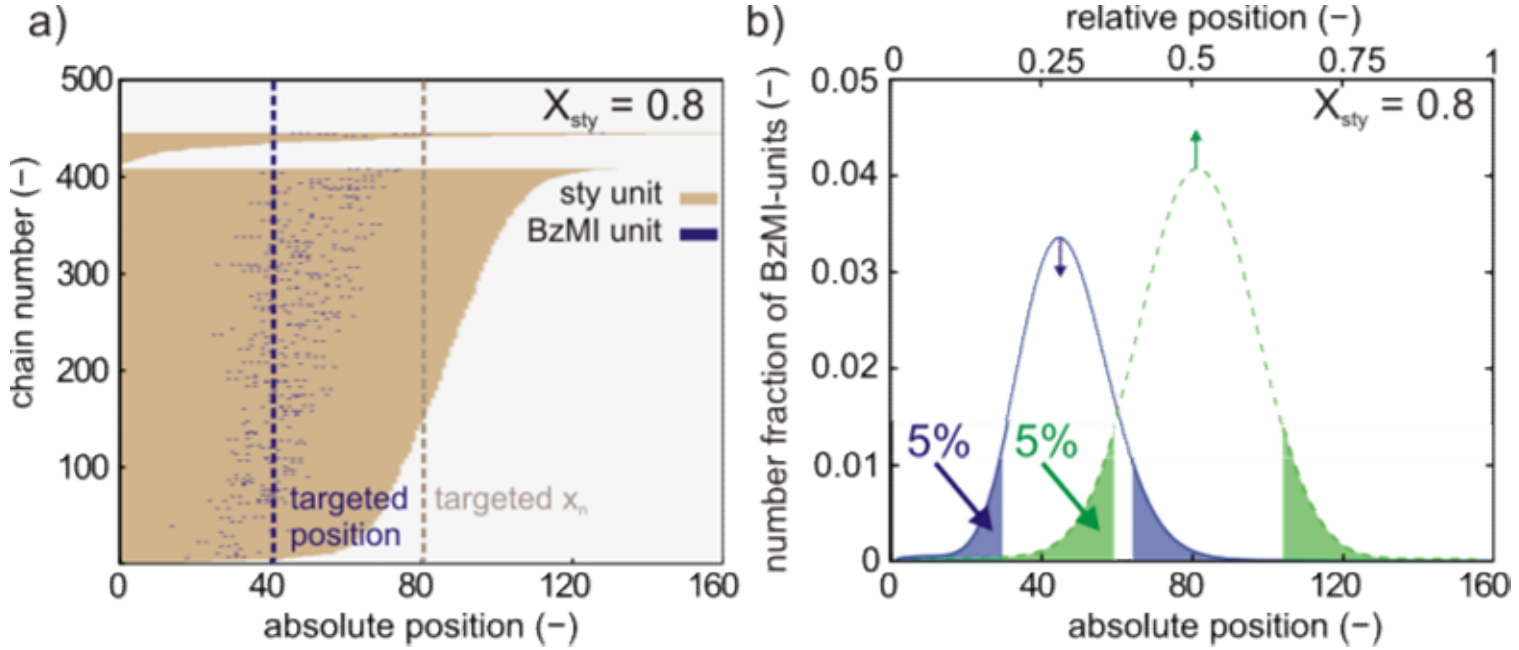
T = 120°C; $[Sty]_0:[R_0X]_0:[BzMI]_{addition\ point}$=100:1:1eq



1 eq BzMI injected at X_{sty} = 0.4

Design of monomer addition program (2)

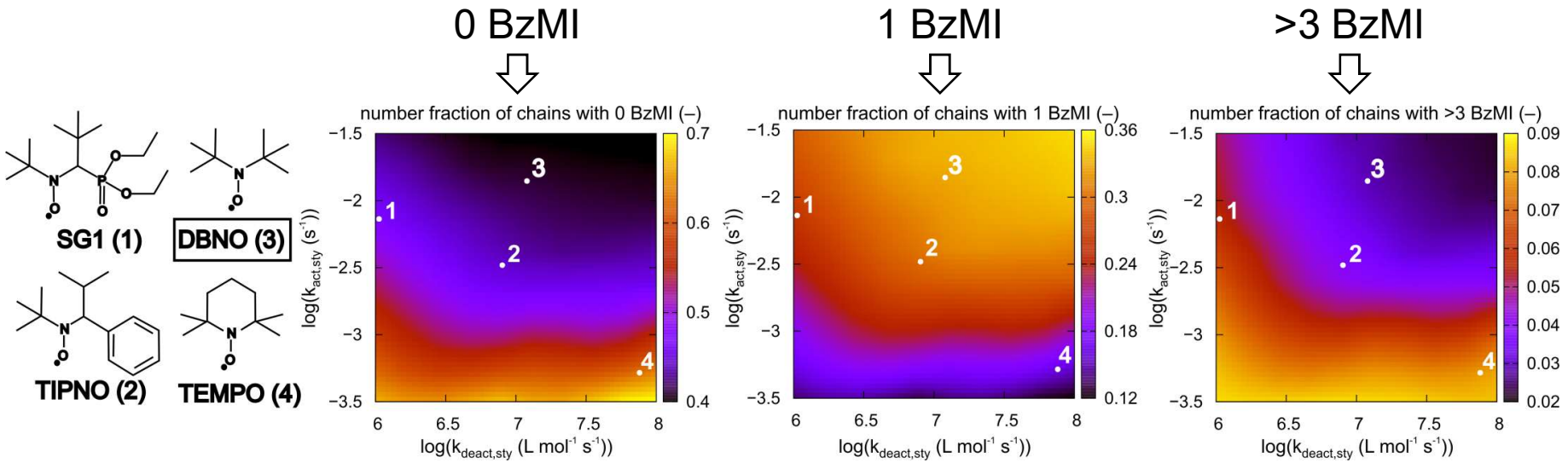
T = 120°C; $[Sty]_0$:$[R_0X]_0$:$[BzMI]_{addition\ point}$=100:1:1eq



half of total styrene amount is added initially; at X_{sty}= 0.80 all of the BzMI is added; at X_{sty} = 0.90 remaining amount of styrene is added

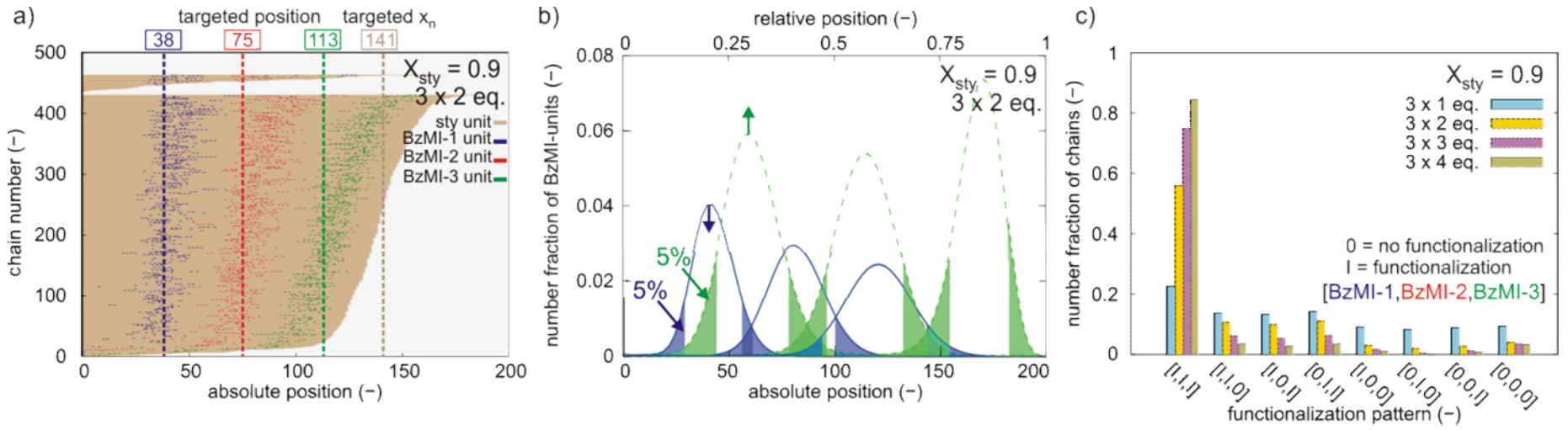
Selection of nitroxide

T = 120°C; $[sty]_0/[BzMI]_{AP}/[X]_0/[BPO]_0$=100/1/1/0.71



Improved BzMI-unit distribution along chains with DBNO

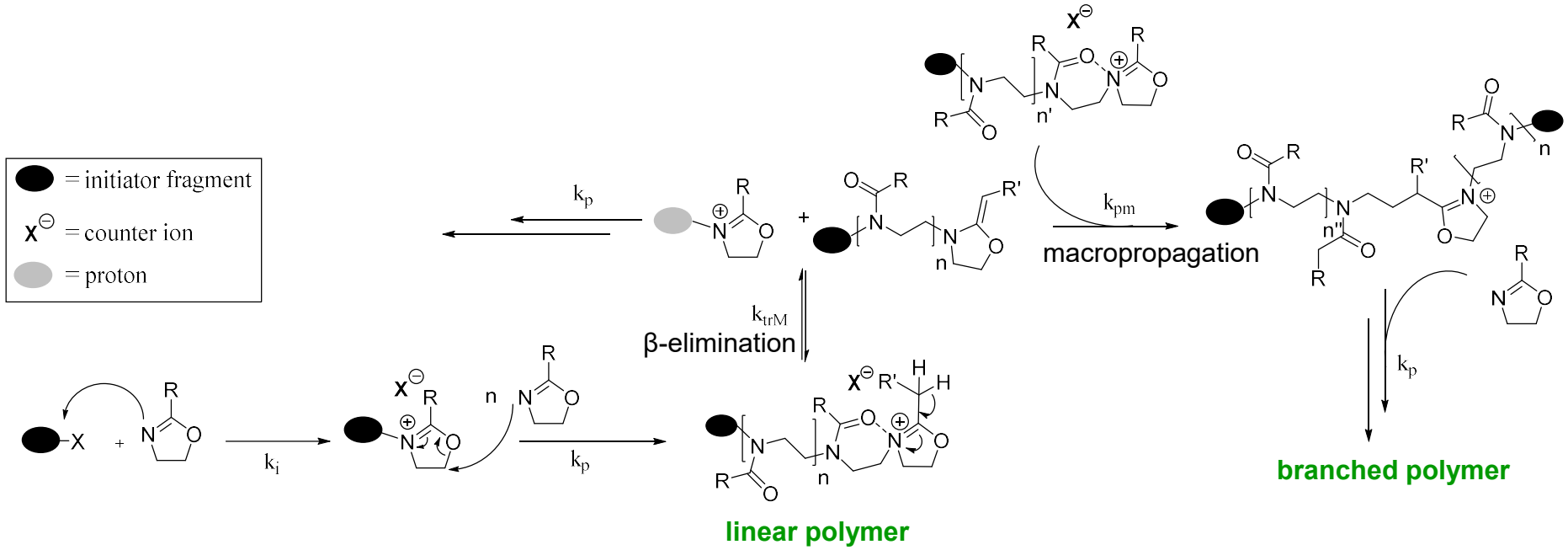
Design of sequence controlled copolymer synthesis



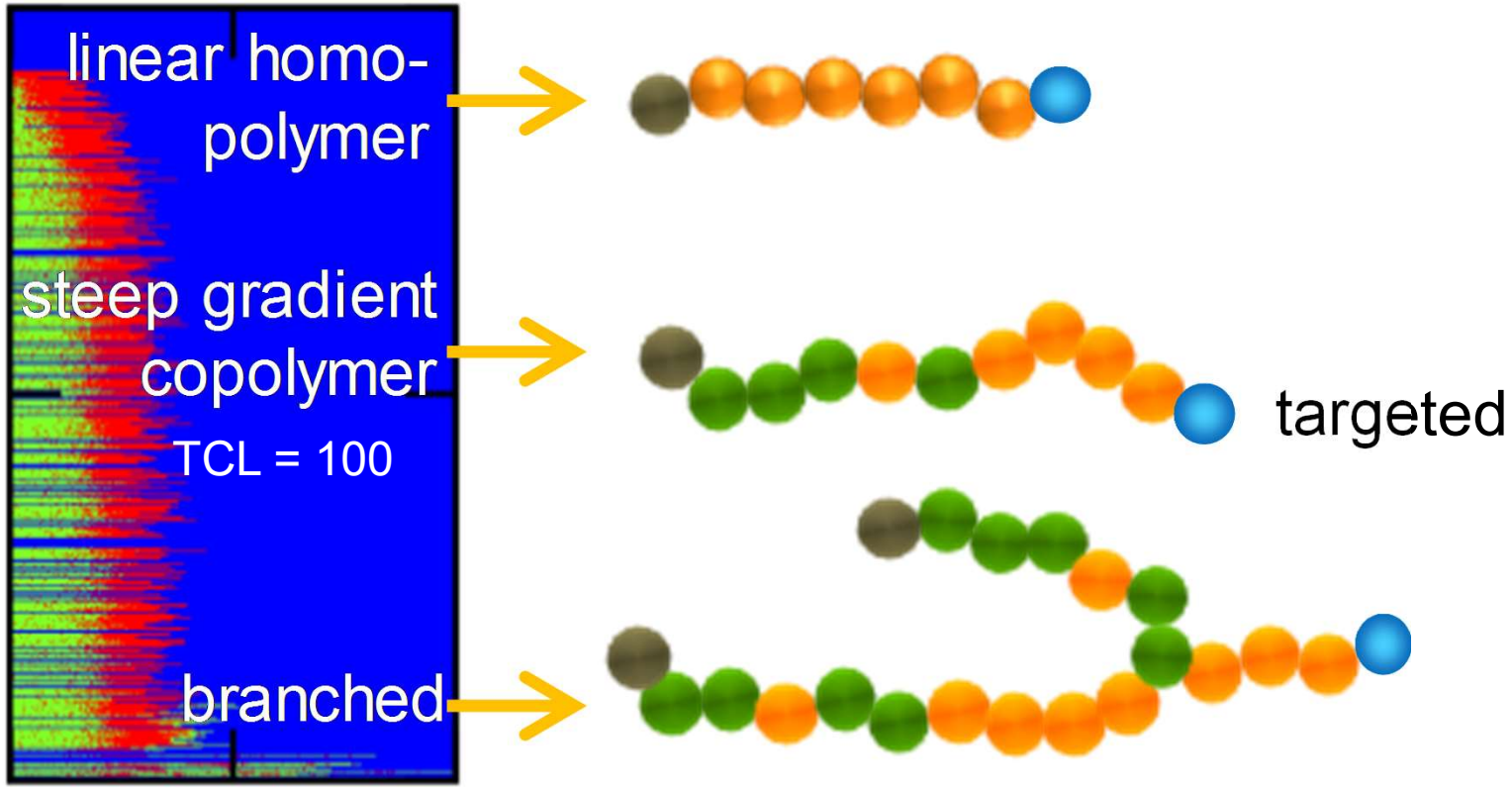
NMP styrene with 3 BzMI additions ; 120°C; $[Sty]_0$:$[R_0X]_0$:$[BzMI\text{-}1]_{AP1}$:$[Sty]_{AP2}$: $[BzMI\text{-}2]_{AP3}$:$[Sty]_{AP4}$:$[BzMI\text{-}3]_{AP5}$:$[Sty]_{AP6}$ = 47:1:eq.:45:eq.:45:eq.:13; eq. each time defined with respect to R_0X; addition point (AP) 1,3 and 5 at X_{sty} = 0.8 and addition point 2, 4 and 6 at X_{sty} = 0.9

Gradient copoly(2-oxazolines) via CROcoP

Cationic Ring-Opening coPolymerization (CROcoP) of MeOx and PhOx initiated by MeOTs in acetonitrile



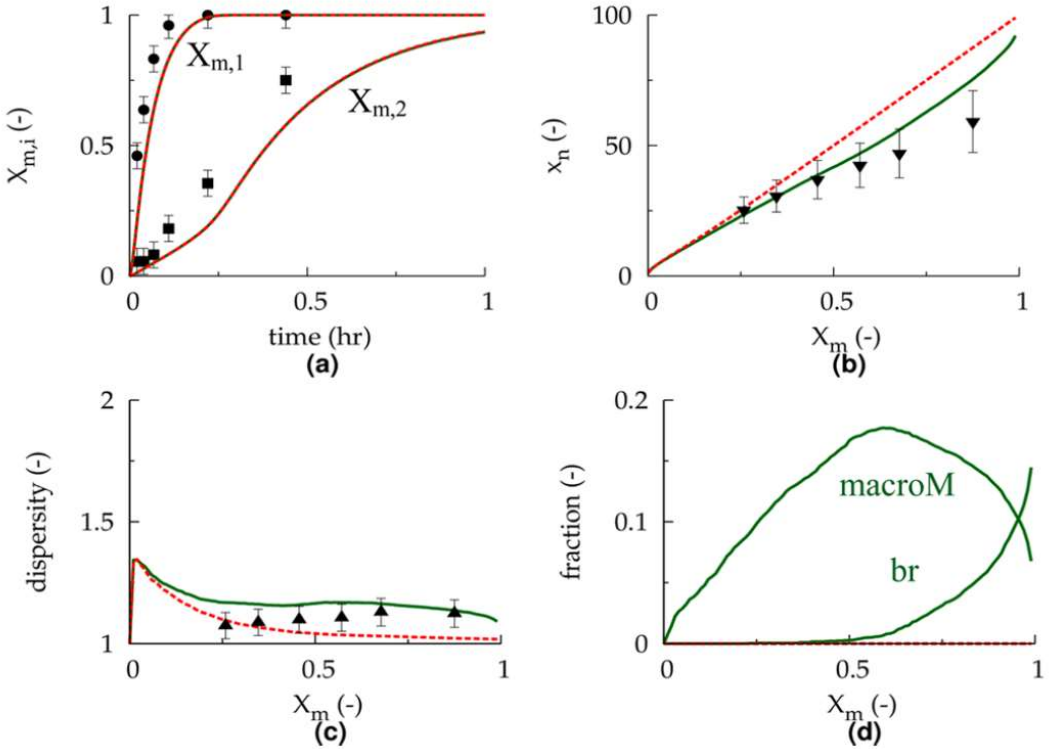
Target: steep MeOx-PhOx gradient



Effect of chain transfer in CROcoP (1)

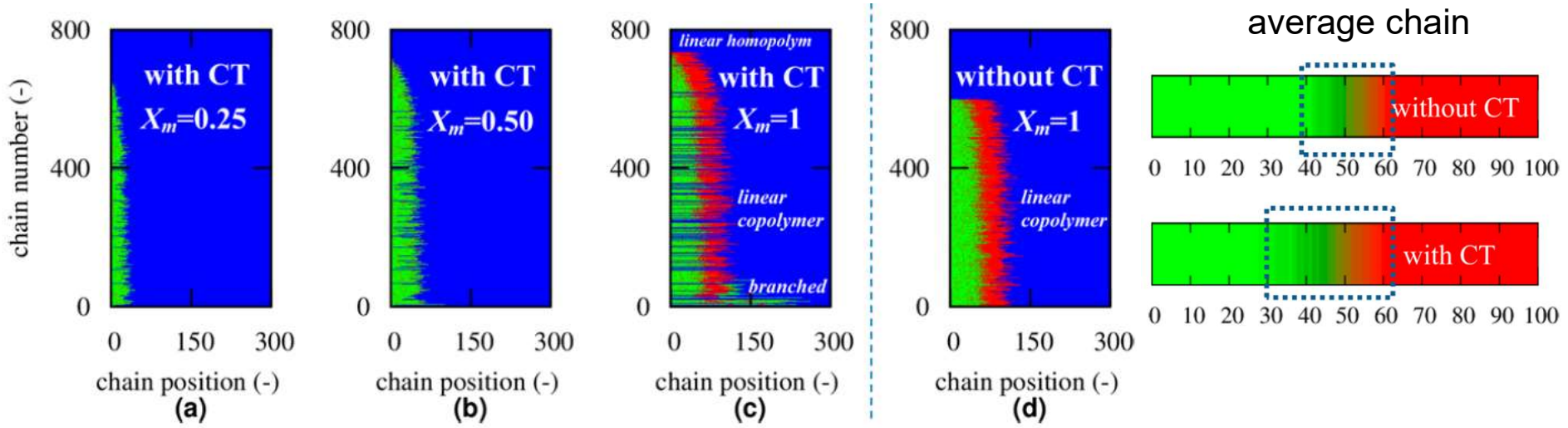
T= 140 °C; $[MeOx]0:[PhOx]_0$: $[MeOTs]_0$ = 50:50:1; $[MeOx]_0 + [PhOx]_0$ = 3 mol L^{-1}; acetonitrile

1 (MeOx), 2 (PhOx)

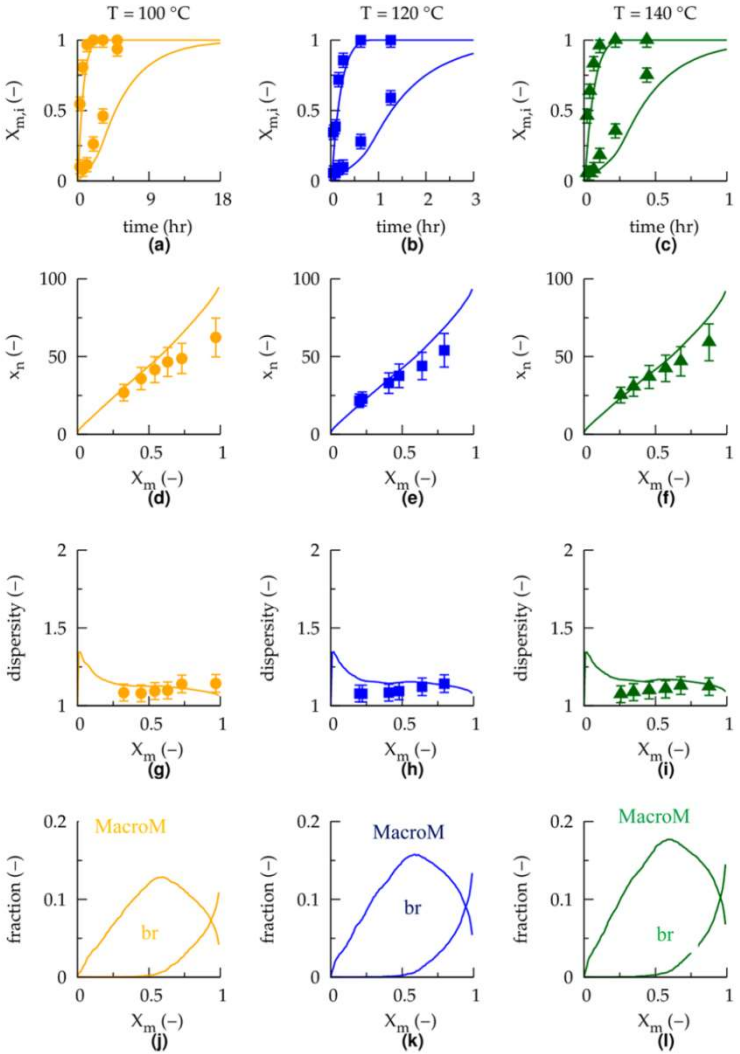


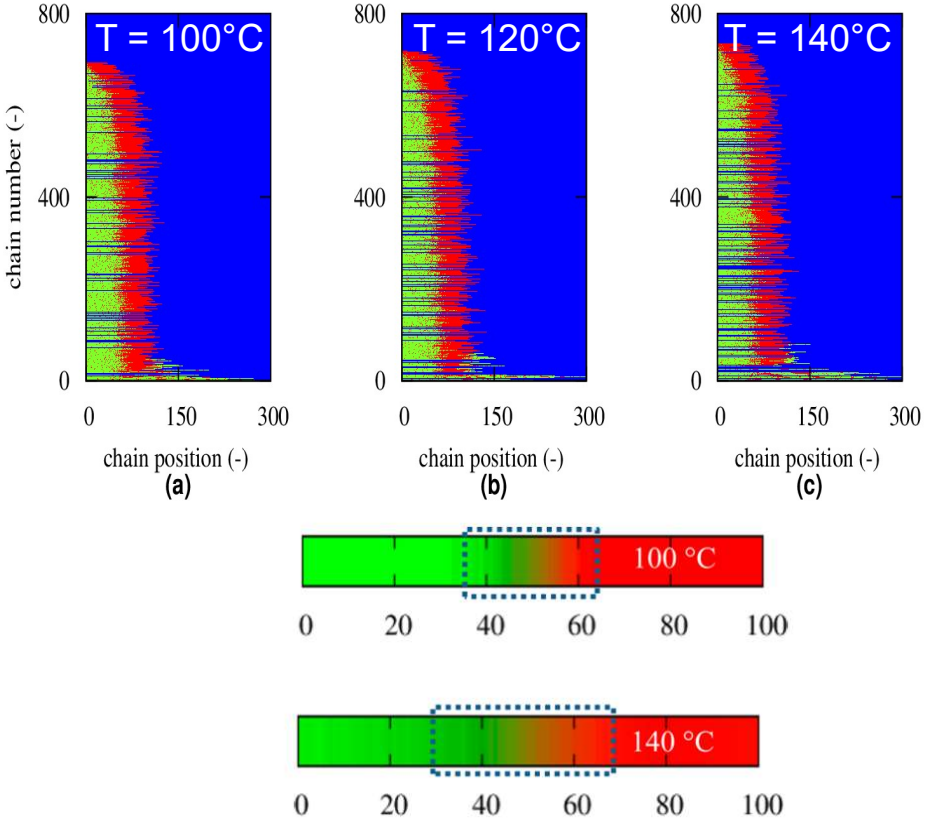
Effect of chain transfer in CROcoP (2)

T= 140 °C; [MeOx]0:[PhOx]$_0$: [MeOTs]$_0$ = 50:50:1; [MeOx]$_0$ + [PhOx]$_0$ = 3 mol L−1; solvent: acetonitrile



Effect of temperature





Conclusions

- Matrix-based kinetic Monte Carlo modeling enables vizualization of the complete microstructure for each individual macromolecule and is a powerful tool to understand and improve controlled polymerization processes

- Complemented with ab initio calculations and combined with experimental studies the developed modeling tools allow a detailed exploration of a given polymer chemistry

Acknowledgements

- national collaborations
  - Prof. F. Du Prez
  - Prof. R. Hoogenboom
  - Prof. Ph. Dubois
  - Prof. T. Junkers
- International collaborations
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  - Prof. C. Barner-Kowollik
  - Prof. M. Coote
  - Prof. R.A. Hutchinson
  - Prof. M.F. Cunningham
  - Prof. M.J. Monteiro
  - Dr. J.F. Lutz

Thank you for your attention!!!